PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2002-143615
(43)Date of publication of application : 21.05.2002

(51)Int.Cl. B01D 39/20
B01D 46/00
B01J 35/04
C04B 38/06
F01N 3/02

(21)Application number : 2000-341644
(22)Date of filing : 09.11.2000

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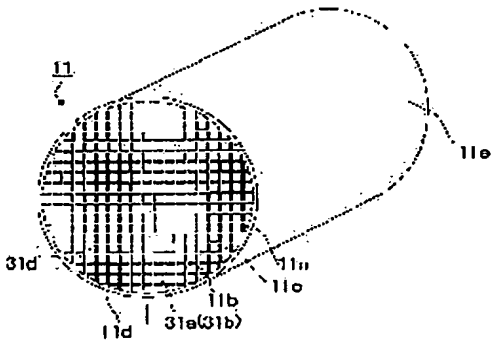
(54) POROUS CERAMIC HONEYCOMB STRUCTURAL BODY

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a honeycomb structural body capable of highly efficiently collecting fine particles in an exhaust gas with the pressure loss decreased and the strength secured.
SOLUTION: The porous honeycomb structural body is constituted so that cell opening part both ends are alternately sealed and the exhaust gas is passed through the fine pores of a cell wall to the adjacent cell to collect the fine particles contained in the exhaust gas on the cell wall and is composed of a cordierite composition and is controlled to have 60-80% porosity of the cell wall, 15-25 μm average fine pore diameter and ≥25% total fine pore volume in 20-40 μm fine pore diameter. The filter surface area per unit volume is controlled to 7-13 cm2/cm3.



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CLAIMS

[Claim(s)]
[Claim 1]****** cell opening both ends by turns, and pass fine pores of a cell wall and exhaust gas is passed to an adjacent cell, Are a porosity honeycomb structured body which is caught

with a cell wall and which consists of a cordierite presentation, and, in porosity of a cell wall, an average pore size particles contained in exhaust gas 60 to 80% at 15-25 micrometers. A porosity ceramic honeycomb structured body, wherein the total pore volume with a pole diameter of 20-40 micrometers is not less than 25% of whole pore volume.
[Claim 2]The porosity ceramic honeycomb structured body according to claim 1, wherein filter surface products per unit volume are 7-13-cm^2/cm^3.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to the porosity honeycomb structured body which catches the particles in the exhaust gas discharged from a diesel engine, for example and which consists of a cordierite presentation.
[0002]
[Description of the Prior Art]In order to call for reduction of the toxic substances contained in the exhaust gas discharged from engines, such as a car, and to respond to this from the preservation side of local environment or earth environment, the catalytic converter for exhaust gas purification is used. One of the catalytic converter of this has a ceramic honeycomb catalyst converter. In order to catch these days the particles contained in the exhaust gas from a diesel engine, The exhaust gas purifying filter which ******(ed) the both ends of the cell opening of this honeycomb structured body by turns has been used using the porosity ceramic honeycomb structured body (henceforth [a "porosity ceramic honeycomb structured body" is omitted and] a "honeycomb structured body") which consists of a cordierite presentation.
[0003]Drawing 1 is a perspective view of a honeycomb structured body, and drawing 2 is a cross section of an example of the exhaust gas purifying filter 10 which used the honeycomb structured body 11 of drawing 1. As shown in drawing 1 and drawing 2, the honeycomb structured body 11 is usually approximately cylindrical, It has the countless cell 11c formed with the peripheral wall 11a and the cell wall 11b which intersects perpendicularly with the inner circumference side of this peripheral wall 11a respectively, and the inflow side of the cell 11c closes the end face by the side of [11e] 11 d and an outflow with the sealing agents 31a and 31b by turns. And the honeycomb structured body 11 is stored in the stowage container 12, it is arranged so that the peripheral wall 11a may stick it with the stowage container 12, and it is grasped in the end face so that it may not move while in use by the gripping members 23a and 23b.
[0004]An exhaust-air-purification operation with the exhaust gas purifying filter 10 is performed as follows. Exhaust gas flows from the cell 11c as for which the inflow side of the honeycomb structured body 11 is carrying out the opening at 11 d (10a shows), and after it passes the fine pores formed in the cell wall 11b, it is discharged from the outflow side 11e (10b shows). And when particles contained in exhaust gas pass to an adjacent cell from the fine pores which

continue within the cell wall 11b, they are filtered, and they are caught. When the quantity of the particles caught increased, and fine pores are got blocked by particles and use for an engine, back pressure increases. For this reason, when the caught particles exceed a constant rate, it is necessary to suppress the load increase to the engine by the increase in back pressure by removing particles. Since particles are the inflammabilities of a fixed-carbon-content ingredient and the soluble organic component which can dissolve in an organic solvent, if it heats in temperature of not less than about 650 **, they will burn. Then, particles are made to afterburn using heating methods, such as an electric heater, a burner, and a hot wind, and the exhaust gas purifying filter 10 is reproduced.

[0005]This exhaust gas purifying filter 10 is required for it to be efficient and to catch the particles contained in exhaust gas while in use, and to make pressure loss low and to lessen load to an engine. However, this collection efficiency and pressure loss have an opposite relation, if it is going to make collection efficiency high, pressure loss will increase, and if pressure loss is made low, collection efficiency will come to get worse. For this reason, in the following conventional technology, providing the filter of high collection efficiency and a low-pressure power loss is indicated by adjusting the fine pores which exist in a filter.

[0006]JP,61-54750,B has a statement that a high-collection-efficiency type to a low collection efficiency type can apply by controlling the porosity and parallel pole diameter of a honeycomb structured body. And the open porosity (porosity) and the average stoma size (average pore size) within the zone limited as a suitable example in this JP,61-54750,B in the boundary to which point 1-5-6-4 of page [20th] drawing 8 is connected are indicated. Here the point 1 Open porosity 58.5 capacity %, and average stoma 1 micrometer in diameter. As for the point 5, open porosity 62.0 capacity %, average stoma 15 micrometers in diameter, and the point 4 of open porosity 39.5 capacity %, average stoma 15 micrometers in diameter, and the point 6 are 1 micrometer in open porosity 90.0 capacity % and average stoma diameter.

[0007]By the honeycomb structured body which becomes JP,9-77573,A from cordierite. Porosity is carried out 62 to 75%, and the fine pores of 25-40 micrometers and a cell wall are preferably made into a 5-40 micrometers stoma and a 40-100-micrometer osculum for an average pore size 55 to 80%, and there is a statement to which it is supposed highly that pressure loss can be made low about collection efficiency considering the number of stomata as five to 40 times of the number of osculums.

[0008]On the other hand, the particles contained in exhaust gas are caught by supporting a catalyst in the side of a cell wall, and fine pores, and detoxicating a toxic substance has also been performed. For example, to JP,9-158710,A. In the filter using the honeycomb structured body which has adhered the coating material containing high specific surface area material particles in the side of a cell wall, and fine pores in the cordierite presentation of a low thermal expansion coefficient, High specific surface area material particles, such as as much activated alumina as possible, are supported with the porosity of the cell wall of a filter after supporting high specific surface area material being carried out, and an average pore size being 5-35 micrometers 40 to 65% in a filter, and there is a statement to which it is supposed that pressure loss can be made low.

[0009]And so that it may face manufacturing a porous ceramic filter and the not less than 150-micrometer particle of a talc powder constituent and a silica powder ingredient which is a cordierite-ized raw material may become 3 or less % of the weight of the whole raw material at JP,7-38930,B, And the art adjusted so that the particle of 45 micrometers or less of these both ingredients may become 25% of the whole is indicated. In order [which can carry out things] according to this art to be able to control formation of fine pores smaller than 10 micrometers and bigger fine pores than 100 micrometers and to increase the fine pores which are 10-50 micrometers, Manufacture of a filter with long low pressure loss and catching time is attained with high collection efficiency maintained, and the pore volume 10% or less and whose diameter the pore volume of not less than 100 micrometers is 10-50 micrometers in diameter as for the porous ceramic filter has the statement that porosity is not less than 65%, 45 to 60%.

[0010]

[Problem(s) to be Solved by the Invention]However, there are the following problems in said

conventional ceramics filter. That is, when this invention persons gave it a try, it was difficult to provide the filter which reconciled the pressure loss and collection efficiency which are the opposite characteristic, and also intensity.
[0011]There was a problem that art given [said] in JP,61-54750,B has a small average pore size, the pressure loss at the time of exhaust gas passage becomes large by a relation with porosity, and fine pores were plugged up by plugging of particles and catalyst support, and ventilation resistance became large.
[0012]Since art given [said] in JP,9-77573,A had the average pore size as large as 25-40 micrometers, more detailed particles penetrated and there was a problem that collection efficiency fell. Since the average pore size was large, the mechanical strength fell and there was also a problem of being easy to damage at the time of an assembly and use.
[0013]On the other hand, when art given [said] in JP,9-158710,A had porosity as small as 40 to 65%, and the pressure loss at the time of exhaust gas passage became large by a relation with a pole diameter and a catalyst was supported, there was a problem that fine pores were plugged up and pressure loss became large.
[0014]And when the art of JP,7-38930,B had porosity as small as 45 to 60%, and the pressure loss at the time of exhaust gas passage became large by a relation with a pole diameter and a catalyst was supported, there was a problem that fine pores were plugged up and pressure loss became large.
[0015]It was difficult to satisfy the pressure loss of a filter, particle collection efficiency, and intensity to conventional technology, as stated above, and it was very difficult with the filter which has especially porosity not less than 60%. Therefore, even if porosity is not less than 60%, there is a technical problem of this invention in obtaining the honeycomb structured body of the high intensity which can catch the particles in exhaust gas efficient, is assembled further, and is not damaged at the time or the time of use, while maintaining a low-pressure power loss.
[0016]
[Means for Solving the Problem]In order that a size of fine pores which exist in a filter might be examined and pore volume with a pole diameter of 20-40 micrometers might reconcile pressure loss, collection efficiency, and intensity, this invention persons found out acting effectively and thought out to this invention.
[0017]Namely, this invention ****** cell opening both ends by turns, and pass fine pores of a cell wall and exhaust gas is passed to an adjacent cell, It is a porosity honeycomb structured body which catches particles contained in exhaust gas with a cell wall and which consists of a cordierite presentation, It is a porosity ceramic honeycomb, wherein porosity of said cell wall is 60 to 80%, an average pore size is 15-25 micrometers and the total pore volume with a pole diameter of 20-40 micrometers is not less than 25% of whole pore volume. And in said porosity ceramic honeycomb structured body, it is preferred that filter surface products per unit volume are 7-13-cm^2/cm^3.
[0018]Next, a reason for composition of this invention is explained.
(Porosity) A porosity ceramic honeycomb structured body of this invention, Since the total pore volume with a pole diameter of 20-40 micrometers is making [in porosity of a cell wall] it not less than 25% of whole pore volume 60 to 80% in addition to 15-25 micrometers of average pore sizes, although porosity is as high as 60 to 80%, A honeycomb structured body of high collection efficiency and high intensity is obtained maintaining a low-pressure power loss. Here, when pressure loss at the time of exhaust gas passage becomes it large that porosity of a cell wall is less than 60% by a relation with a pole diameter and a catalyst is supported, the holding amount decreases. On the other hand, if porosity exceeds 80%, at the same time as intensity falls, collection efficiency of particles will fall. Therefore, porosity is made into 60 to 80%. Preferably, porosity is 60 to 70%.
[0019](Average pore size) Pressure loss at the time of exhaust gas passage becomes large by a relation with porosity, and an average pore size is closed with less than 15 micrometers by plugging of particles, and catalyst support, and ventilation resistance becomes large. On the other hand, if an average pore size exceeds 25 micrometers, intensity's falling and more detailed particles will penetrate and collection efficiency will fall.

[0020](Pore volume) Fine pores which it is good to increase fine pores with a pole diameter of not less than 20 micrometers for making pressure loss small, and exceed 40 micrometers on the other hand reduce becoming a case where it becomes a starting point of destruction and intensity falls, and collection efficiency of particles. For this reason, the total pore volume with a pole diameter of 20–40 micrometers is required for not less than 25% of whole pore volume. Porosity, an average pore size, and a pole diameter are measured using a mercury pressure ON type porosimeter.
[0021](Filter surface product per unit volume) A filter surface product means surface area of a cell wall. When a filter surface product per unit volume is less than 7-cm^2/cm^3 in a honeycomb structured body, Ventilation resistance at the time of exhaust gas passing to an adjacent cell becomes large, and pressure loss becomes large on the contrary because cell density will become high if pressure loss becomes large and exceeds 13-cm^2/cm^3.
[0022]
[Embodiment of the Invention]Hereafter, an embodiment of the invention is described in detail. The honeycomb structured body 11 shown in drawing 1 and drawing 2 was produced as follows. (Adjustment in the end of precursor powder) Adjust powder, such as kaolin, talc, silica, hydroxylation aluminum, and alumina, and chemical composition with a mass ratio. SiO_2: 48–52%, aluminum$_2O_3$:33–37%, MgO: 12–15%, CaO: 0 to 0.05%, Na_2O : 0 to 0.05%, K_2O : 0 to 0.05%, TiO_2:0–1.0%, Fe_2O_3:0–1.0%, PbO: It was considered as the precursor powder end of the nature ceramics of cordierite containing 0 to 0.1%, and P_2O_5:0–0.2%.
[0023]To (addition of a forming assistant and an ostomy agent and refining of a plastic matter), next the precursor powder end of these nature ceramics of cordierite, as a forming assistant as methyl cellulose, hydroxypropylmethylcellulose, and an ostomy agent, Quantity, such as graphite, wheat flour, and starch, was changed, and it added, and mixed enough by dry type. Subsequently, the water of the stipulated amount was poured in, still more sufficient kneading was performed, and the plastic matter in which extrusion molding is possible was produced.
[0024](Extrusion molding) Next, the Plastic solid in which the peripheral wall and the cell wall were formed in one of the publicly known extrusion method in this plastic matter and which has honeycomb structure with a 143.8 mm[in diameter] x length of 152.4 mm was fabricated. The Plastic solid which changes the size of a metallic mold and has a filter surface product per various unit volume was acquired.
[0025](Calcination) Next, the Plastic solid which has this honeycomb structure was calcinated with the maximum temperature of 1405 ** using the batch type firing furnace. The cell wall thickness of the obtained baking body was 0.12–0.60 mm, the cell density 75 – 400cpsi.
[0026](******) Next, the exhaust-gas-flow ON side of this honeycomb structured body 11 ****** an 11-d cell every piece, and it **** [chisel] in the exhaust-gas-flow appearance side 11e about the cell as for which an inflow side is not ******(ing) at 11 d. The ****** material is just an existing charge of a ceramic material with a heat resistance [, such as cordierite, alumina, and zirconia,] of not less than 1000 **, and the adhesives made from ceramics may be sufficient as it. And it becomes the exhaust gas purifying filter 10 which there is little pressure loss, and intensity can be secured, and can catch the particles in exhaust gas efficient, or can improve a purification function from immediately after engine start further by storing in the stowage container 12.
[0027]and (%) and the ratio of the total with (%) and the porosity of the cell wall 11b, an average pore size (micrometer), and a pole diameter of 20–40 micrometers pore volume to whole pore volume, and the filter surface product per unit volume (cm^2/cm^3) were boiled, attached and measured about the honeycomb structured body 11 produced by ******(ing). The filter surface product per unit volume measured and computed cell wall thickness and a cell pitch. The result is shown in Table 1 at order with small porosity (%). Here, for measurement of porosity, an average pore size, and a pole diameter, auto pore III9410 made from Micromeritics was used, and it measured with the method of mercury penetration to it.
[0028]

(Table 1)
No. classification Porosity Average pore size the ratio of the total fine-pores filter surface product (%) (micrometer) capacity with a pole diameter of 20-40 micrometers to whole pore volume — (%) (cm^2/cm^3) 01 comparative example 1 54.5 7.7 4.1 5.902.Comparative example 2 56.7 13.1 18.6. 13.503 Comparative example 3 56.8 14.9. 22.5 6.504 Example of an invention 1 60.8. 19.8 49.6 6.805 comparative example . 4 64.0 11.2 15.4 5.706. Comparative example 5 64.3 11.7 10.1. 6.107 Example of invention 2 66.0 17.0. 30.6 8.008 Comparative example 6 66.2. 14.5 26.6 13.509 comparative example . 7 66.6 12.0 9.4 5.710. Example of an invention 3 66.6 19.5 26.4. 10.811 Example 4 of an invention 67.2 16.0. 27.3 7.812 Example of an invention 5 67.2. 21.8 42.0 8.313 Comparative example 8 70.0 13.4 11.4 6.514 Comparative example 9 70.2 27.0 44.8 8.315 Example of an invention 6 70.4 18.8 45.7 14.016 Comparative example 10 74.8 13.7. 17.0 6.017 Example of an invention 7 78.9 17.3 31.7 11.018 Comparative example 11 82.8 13.7 17.0 6.0[0029] Next, the time of using the honeycomb structured body 11 with pressure loss test equipment (not shown) with 7.5 Nm of (a) air flow rate ^{3} / min, After supporting the differential pressure by the side of [11e] 11 d and an outflow and an inflow side (c) catalyst after throwing in with the differential pressure by the side of [11e] 11 d and an outflow, and an inflow side (b) particle diameter of 0.042 micrometer carbon powder by 3 g/h for 2 hours, the inflow side at the time of 7.5-Nm^3/min measured the differential pressure by the side of [11e] 11 d and an outflow. And the inflow side searched for pressure loss (mmAq) by the differential pressure by the side of [11e] 11 d and an outflow. Evaluation of pressure loss about (a) honeycomb structured body 11 independent (the next table 2 shows as a "carrier") one. By setting to NG what makes less than 230 mmAq A and exceeds (O) and 250mmAq by making (O) and 230 - 250mmAq into good, by (x) about (b) carbon powder. By setting to NG what makes less than 380 mmAq A and exceeds (O) and 400mmAq by making (O) and 380 - 400mmAq into good, by (x) about the (c) catalyst. It carried out by (x) by setting to NG what makes less than 280 mmAq A and exceeds (O) and 300mmAq by making (O) and 280 - 300mmAq into good. The collection efficiency (%) after throwing in carbon powder with a particle diameter of 0.042 micrometer by 3 g/h for 2 hours was measured. Society of Automotive Engineers of Japan Based on automobile standard (JASO) M505-87, the compression disruptive strength (MPa) of the A-axis was measured about the honeycomb structured body 11, respectively. The result is shown in Table 2.
[0030]
(Table 2)
No. Evaluation collection efficiency A axial compression disruptive strength (a) carrier (b) carbon powder (c) catalyst (%) (MPa) 01 of classification pressure loss Comparative example 1 x x x 100 8.802 Comparative example 2 O x x 100 7.003 The comparative example 3.O x O 98 6.604 Example of an invention 1. O O O 97 5.005 Comparative example 4. x x x 100 6.206 comparative example . 5 x x x 100 Example of 5.607 invention . 2 O O O 99 3.508 comparative example . 6 O x O 97 5.409 comparative example . 7 x x x 100 Example of 6.510 invention . 3 O O O 97 Example of 4.211 invention . 4 O O O 100 Example of 4.012 inventions . 5 O O O 96 3.013 comparative example . 8 O x O 100 1.814 Comparative example 9 O O O 92 0.815 Example of an invention 6 O O O 97 3.616 comparative-example 10 O x O 98 1.417 Example of an invention 7 O O O 98 2.818 comparative-example 11 O x O 97 0.5[0031]From Table 2, since the total pore volume of 20-40 micrometers is setting [the average pore size] to 15-25 micrometers not less than 25% of whole pore volume, although porosity is enlarged with 60 to 80%, the examples 1-7 of an invention, (a) All have little pressure loss after honeycomb structured body 11 independence, (b) carbon powder injection, and (c) catalyst support. The examples 1-7 of an invention have the high collection efficiency of carbon powder, and A axial compression disruptive strength is also secured. Pressure loss can be lessened more by making the filter surface product per unit volume into 7-13-cm^2/cm^3 especially. On the other hand, the comparative examples 1-11 are also set they to be [any of the pressure loss of ** after (a) honeycomb structured body 11 independence, (b) carbon powder injection, and (c) catalyst support or the collection efficiency of carbon powder, and A axial compression disruptive strength], and are not enough, and the problem is left behind.

[0032]
[Effect of the Invention]Maintaining a low-pressure power loss according to the honeycomb structured body of this invention as explanation in details, above, although porosity is large, intensity can be secured and the particles in exhaust gas can be caught efficient.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1]It is a perspective view of a honeycomb structured body.
[Drawing 2]It is a cross section of an example of the exhaust gas purifying filter 10 using the honeycomb structured body of drawing 1.
[Description of Notations]
11: Honeycomb structured body
11a: Peripheral wall
11b: Cell wall
11c: Cell
11d: Inflow side
11e: Outflow side
12: Stowage container
23a, 23b: Gripping member.

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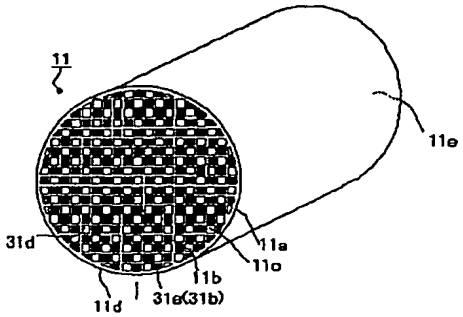
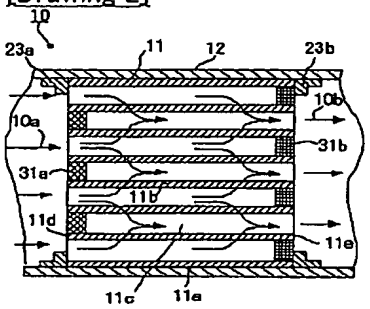
DRAWINGS

[Drawing 1]



[Drawing 2]



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(19)日本国特許庁（ＪＰ）　(12)公開特許公報（Ａ）　(11)特許出願公開番号
特開2002－143615
（P2002－143615A）
(43)公開日　平成14年５月21日(2002.5.21)

(51)Int.Cl.'		識別記号	Ｆ Ｉ		テーマコード'（参考）
Ｂ０１Ｄ	39/20		Ｂ０１Ｄ	39/20	Ｄ　３Ｇ０９０
	46/00	３０２		46/00	３０２　４Ｄ０１９
Ｂ０１Ｊ	35/04	３０１	Ｂ０１Ｊ	35/04	３０１Ｄ　４Ｄ０５８
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Ｆ０１Ｎ	3/02	３０１	Ｆ０１Ｎ	3/02	３０１Ｃ

審査請求　有　請求項の数２　ＯＬ　（全６頁）

(21)出願番号　特願2000－341644(P2000－341644)
(22)出願日　平成12年11月９日(2000.11.9)

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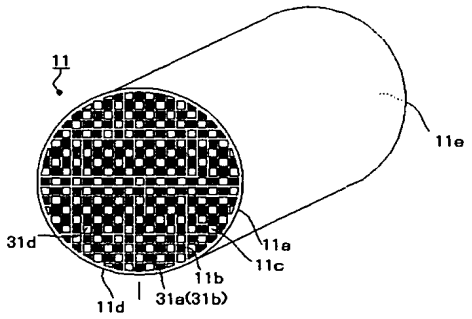
最終頁に続く

(54)【発明の名称】　多孔質セラミックハニカム構造体

(57)【要約】
【課題】　圧力損失を少なくすると共に強度を確保し、また排気ガス中の微粒子を高効率に捕集することのできるハニカム構造体を得る。
【解決手段】　セル開口部両端を交互に目封じして、排気ガスをセル壁の細孔を通過させて隣接セルに流し、排気ガスに含まれる微粒子をセル壁で捕集する、コーディエライト組成からなる多孔質ハニカム構造体であって、セル壁の気孔率が６０～８０%、平均細孔径が１５～２５μｍであって、細孔径２０～４０μｍの総細孔容積が全細孔容積の２５%以上とする。又は、更に単位体積あたりのフィルター表面積を７～１３ｃｍ²／ｃｍ³とする。



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【特許請求の範囲】

【請求項１】　セル開口部両端を交互に目封じして、排気ガスをセル壁の細孔を通過させて隣接セルに流し、排気ガスに含まれる微粒子をセル壁で捕集する、コーディエライト組成からなる多孔質ハニカム構造体であって、セル壁の気孔率が６０～８０%、平均細孔径が１５～２５μmで、細孔径２０～４０μmの総細孔容積が全細孔容積の２５%以上であることを特徴とする多孔質セラミックハニカム構造体。

【請求項２】　単位体積あたりのフィルター表面積が７～１３cm^2／cm^3であることを特徴とする請求項１に記載の多孔質セラミックハニカム構造体。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、例えば、ディーゼルエンジンから排出される排気ガス中の微粒子を捕集する、コーディエライト組成からなる多孔質ハニカム構造体に関する。

【０００２】

【従来技術】地域環境や地球環境の保全面から、自動車などのエンジンから排出される排気ガスに含まれる有害物質の削減が求められ、これに応えるため排気ガス浄化用の触媒コンバータが用いられている。この触媒コンバータのひとつにセラミックハニカム触媒コンバータがある。また、最近はディーゼルエンジンからの排気ガス中に含まれる微粒子を捕集するために、コーディエライト組成からなる多孔質セラミックハニカム構造体（以下、「多孔質セラミックハニカム構造体」を略して「ハニカム構造体」という）を用い、このハニカム構造体のセル開口部の両端を交互に目封じした排気ガス浄化フィルタが使用されてきている。

【０００３】図１はハニカム構造体の斜視図であり、図２は、図１のハニカム構造体１１を用いた排気ガス浄化フィルタ１０の一例の断面模式図である。図１及び図２に示すように、通常、ハニカム構造体１１は略円筒状で、外周壁１１ａと、この外周壁１１ａの内周側に各々直交するセル壁１１ｂにより形成された無数のセル１１ｃを有し、セル１１ｃの流入側１１ｄ、流出側１１ｅの端面を交互に封止材３１ａ、３１ｂで封止されている。そして、ハニカム構造体１１は、収納容器１２内に収納され、その外周壁１１ａが収納容器１２と密着するべく配置され、把持部材２３ａ、２３ｂにより、使用中に動かないように端面で把持されている。

【０００４】排気ガス浄化フィルタ１０での排気浄化作用は、以下の通り行われる。排気ガスは、ハニカム構造体１１の流入側１１ｄで開口しているセル１１ｃから流入（１０ａで示す）し、セル壁１１ｂに形成された細孔を通過した後、流出側１１ｅから排出（１０ｂで示す）される。そして、排気ガス中に含まれる微粒子などは、セル壁１１ｂ内で連続する細孔から隣接セルに通過する際に濾過され、捕集される。捕集される微粒子の量が多くなると細孔が微粒子によって詰まり、エンジンに用いた場合に背圧が増加する。このため、捕集された微粒子が一定量を超えたときに微粒子を除去することによって、背圧増加によるエンジンへの負荷増加を抑える必要がある。微粒子は、固定炭素成分と有機溶剤に溶解可能な可溶性有機成分の可燃性であるので、約６５０℃以上の温度に加熱すれば燃焼する。そこで、電気ヒータ、バーナ、熱風などの加熱手段を用いて微粒子を再燃焼させて、排気ガス浄化フィルタ１０を再生している。

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【０００５】この排気ガス浄化フィルタ１０には、使用中に、排気ガスに含まれる微粒子を高効率で捕集すること、圧力損失を低くしてエンジンへの負荷を少なくすることが要求されている。しかしながら、この捕集効率と圧力損失は相反する関係にあり、捕集効率を高くしようとすると圧力損失が増大し、また圧力損失を低くすると、捕集効率が悪化するようになる。このため、下記の従来技術では、フィルタ中に存在する細孔を調整することにより、高捕集効率及び低圧力損失のフィルタを提供することが開示されている。

【０００６】特公昭６１－５４７５０号公報には、ハニカム構造体の気孔率と平行細孔径を制御することで高捕集効率タイプから低捕集効率タイプまで適用できるとの記載がある。そして、この特公昭６１－５４７５０号公報での好適な具体例として、第２０頁の図８の点１－５－６－４を結ぶ境界内で限定される帯域内のオーブンポロシティ（気孔率）及び平均気孔寸法（平均細孔径）が記載されている。ここで点１はオーブンポロシティ５８．５容量%、平均気孔直径１μm、点５はオーブンポロシティ３９．５容量%、平均気孔直径１５μm、点６はオーブンポロシティ６２．０容量%、平均気孔直径１５μm、点４はオーブンポロシティ９０．０容量%、平均気孔直径１μmである。

【０００７】また、特開平９－７７５７３号公報には、コーディエライトからなるハニカム構造体で、気孔率を５５～８０%好ましくは６２～７５%、平均細孔径を２５～４０μm、かつセル壁の細孔を５～４０μmの小孔と４０～１００μmの大孔とし、また小孔の数を大孔の数の５～４０倍として、捕集率を高く、圧力損失を低くできるとする記載がある。

【０００８】一方、セル壁の側面及び細孔内に触媒を担持することで、排気ガスに含まれる微粒子を捕集すると共に有害物質を無害化することも行われてきている。例えば、特開平９－１５８７１０号公報には、低熱膨張係数のコーディエライト組成で、セル壁の側面及び細孔内に高比表面積材料粒子を含むコーティング材料を付着しているハニカム構造体を用いたフィルタにおいて、高比表面積材料を担持した後の、フィルタのセル壁の気孔率を４０～６５%、平均細孔径を５～３５μmとすることで、フィルタになるべく多くの活性アルミナなどの高比

表面積材料粒子を担持すると共に、圧力損失を低くできるとする記載がある。

【０００９】そして、特公平７－３８９３０号公報には、多孔質セラミックフィルタを製造するに際し、コージェライト化原料である、タルク粉末成分とシリカ粉末成分の１５０μｍ以上の粒子が原料全体の３重量%以下となるように、且つこれら両成分の４５μｍ以下の粒子が全体の２５%となるように調整する技術が開示されている。この技術によれば、１０μｍよりも小さな細孔や、１００μｍよりも大きな細孔の形成を制御することができ、１０～５０μｍの細孔を増大させることできるため、高捕集効率を維持したまま低圧損、捕集時間の長いフィルタの製作が可能となり、その多孔質セラミックフィルタは、気孔率が４５～６０%、直径が１００μｍ以上の細孔容積は１０%以下、かつ直径が１０～５０μｍの細孔容積は６５%以上であるという記載がある。

【００１０】

【発明が解決しようとする課題】しかしながら、前記従来のセラミックフィルタにおいては以下の問題がある。即ち本発明者らが実際にやってみると、相反する特性である、圧力損失と捕集効率、更には強度を両立させたフィルタを提供することが困難であった。

【００１１】前記特公昭６１－５４７５０号公報記載の技術は、平均細孔径が小さく、気孔率との関係で排気ガス通過時の圧力損失が大きくなり、また、微粒子の詰まりや触媒担持により細孔が塞がれて通気抵抗が大きくなるという問題があった。

【００１２】前記特開平９－７７５７３号公報記載の技術は、平均細孔径が２５～４０μｍと大きいため、より微細な微粒子が透過してしまい、捕集効率が低下するという問題があった。また、平均細孔径が大きいために、機械的強度が低下し、組立時や使用時に破損し易いという問題もあった。

【００１３】一方、前記特開平９－１５８７１０号公報記載の技術は、気孔率が４０～６５%と小さく、細孔径との関係で排気ガス通過時の圧力損失が大きくなり、また、触媒を担持した場合に細孔が塞がれて圧力損失が大きくなるという問題があった。

【００１４】そして、特公平７－３８９３０号公報の技術は、気孔率が４５～６０%と小さく、細孔径との関係で排気ガス通過時の圧力損失が大きくなり、また、触媒を担持した場合に細孔が塞がれて圧力損失が大きくなるという問題があった。

【００１５】以上述べたように従来技術では、フィルタの圧力損失、微粒子捕集効率、強度を満足させることは難しく、特に気孔率を６０%以上有するフィルタでは極めて困難であった。従って、本発明の課題は、低圧力損失を維持するとともに、気孔率が６０%以上であっても、排気ガス中の微粒子を高効率に捕集することができ、さらには組立て時或いは使用時に破損しない高強度

のハニカム構造体を得ることにある。

【００１６】

【課題を解決するための手段】本発明者らは、フィルタ中に存在する細孔の大きさについて検討を行い、細孔径２０～４０μｍの細孔容積が圧力損失、捕集効率、強度を両立させるために有効に作用することを見出し本発明に想到した。

【００１７】すなわち、本発明は、セル開口部両端を交互に目封じして、排気ガスをセル壁の細孔を通過させて隣接セルに流し、排気ガスに含まれる微粒子をセル壁で捕集する、コーディエライト組成からなる多孔質ハニカム構造体であって、前記セル壁の気孔率が６０～８０%、平均細孔径が１５～２５μｍであって、細孔径２０～４０μｍの総細孔容積が全細孔容積の２５%以上であることを特徴とする多孔質セラミックハニカムである。そして、前記多孔質セラミックハニカム構造体において、単位体積あたりのフィルター表面積が７～１３ｃｍ²／ｃｍ³であることが好ましい。

【００１８】次に、本発明の構成の理由を説明する。

（気孔率）本発明の多孔質セラミックハニカム構造体は、セル壁の気孔率が６０～８０%、平均細孔径１５～２５μｍに加え、細孔径２０～４０μｍの総細孔容積が全細孔容積の２５%以上としているため、気孔率が６０～８０%と高いにも拘わらず、低圧力損失を維持しつつ、高捕集効率、高強度のハニカム構造体が得られるのである。ここで、セル壁の気孔率が６０%未満であると、細孔径との関係で排気ガス通過時の圧力損失が大きくなり、また触媒を担持した場合その担持量が少なくなる。一方、気孔率が８０%を超えると、強度が低下するのと同時に微粒子の捕集効率が低下する。従って、気孔率は６０～８０%とする。好ましくは、気孔率は６０～７０%である。

【００１９】（平均細孔径）平均細孔径が１５μｍ未満では、気孔率との関係で排気ガス通過時の圧力損失が大きくなり、また微粒子の詰まりや触媒担持により塞がれて通気抵抗が大きくなる。一方、平均細孔径が２５μｍを超えると、強度が低下するのとより微細な微粒子が透過して捕集効率が低下する。

【００２０】（細孔容積）圧力損失を小さくするには細孔径２０μｍ以上の細孔を多くするのが良く、一方、４０μｍを超える細孔は破壊の起点となって強度が低下する場合となることと、微粒子の捕集率を低下させる。このため、細孔径２０～４０μｍの総細孔容積が全細孔容積の２５%以上が必要である。なお、気孔率、平均細孔径、細孔径は、水銀圧入式ポロシメータを用いて測定する。

【００２１】（単位体積あたりのフィルター表面積）フィルター表面積とは、セル壁の表面積をいう。ハニカム構造体において単位体積あたりのフィルター表面積が７ｃｍ²／ｃｍ³未満の場合は、圧力損失が大きくなり、１

３ｃｍ²／ｃｍ³を超えるとセル密度が高くなることで、排気ガスが隣接セルに通過する際の通気抵抗が大きくなり、かえって圧力損失が大きくなる。

【００２２】

【発明の実施の形態】以下、発明の実施の形態を詳細に説明する。図１及び図２に示すハニカム構造体１１を以下のようにして作製した。

（原料粉末の調整）カオリン、タルク、シリカ、水酸化アルミ、アルミナなどの粉末を調整して、化学組成が質量比で、SiO_2：４８～５２%、Al_2O_3：３３～３７%、ＭｇＯ：１２～１５%、ＣａＯ：０～０．０５%、Na_2O：０～０．０５%、K_2O：０～０．０５%、TiO_2：０～１．０%、Fe_2O_3：０～１．０%、ＰｂＯ：０～０．１%、P_2O_5：０～０．２%を含むコーディエライト質セラミックの原料粉末とした。

【００２３】（成形助剤及び造孔剤の添加と、坏土の精製）次に、このコーディエライト質セラミックの原料粉末に対し、成形助剤としてメチルセルロースとヒドロキシプロピルメチルセルロース、造孔剤として、グラファイト、小麦粉、でん粉などの量を変えて添加し、乾式で十分混合した。次いで、規定量の水を注入して更に十分な混練を行い、押出成形可能な坏土を作製した。

【００２４】（押出成形）次に、この坏土を公知の押出成形法により、外周壁とセル壁とが一体に形成された、直径１４３．８ｍｍ×長さ１５２．４ｍｍのハニカム構造を有する成形体を成形した。なお、金型の寸法を変更して各種単位体積あたりのフィルター表面積を有する成形体が得られるようにした。

＊【００２５】（焼成）次に、このハニカム構造を有する成形体を、バッチ式焼成炉を用いて最高温度１４０５℃で焼成を行った。得られた焼成体のセル壁厚は０．１２～０．６０ｍｍ、セル密度７５～４００ｃｐｓｉであった。

【００２６】（目封じ）次に、このハニカム構造体１１の排気ガス流入側１１ｄのセルを一個おきに目封じし、排気ガス流出側１１ｅでは流入側１１ｄで目封じしてないセルについてのみ目封じする。目封じ材はコーディエライト、アルミナ、ジルコニアなど、１０００℃以上の耐熱性のあるセラミック材料であれば良く、またセラミック製の接着剤でもよい。そして、収納容器１２内に収納することで、圧力損失が少ないと共に強度が確保され、排気ガス中の微粒子を高効率に捕集し、又は更に、エンジン始動直後から浄化機能を高めることのできる、排気ガス浄化フィルタ１０となる。

【００２７】そして、目封じして得られたハニカム構造体１１について、セル壁１１ｂの気孔率（%）、平均細孔径（μｍ）、細孔径２０～４０μｍの総細孔容積と全細孔容積の比（%）、単位体積あたりのフィルター表面積（ｃｍ²／ｃｍ³）をについて測定した。尚、単位体積あたりのフィルター表面積は、セル壁厚とセルピッチを測定して算出した。その結果を、表１に気孔率（%）の小さい順に示す。ここで、気孔率、平均細孔径、細孔径の測定には、Micromeritics社製のオートポアIII９４１０を使用し、水銀圧入法で測定した。

【００２８】

＊（表１）

No.	区分	気孔率 (%)	平均細孔径 (μm)	細孔径20～40μmの総細孔容積と全細孔容積の比(%)	ﾌｨﾙﾀｰ表面積 (cm²/cm³)
01	比較例 1	54.5	7.7	4.1	5.9
02	比較例 2	56.7	13.1	18.6	13.5
03	比較例 3	56.8	14.9	22.5	6.5
04	発明例 1	60.8	19.8	49.6	6.8
05	比較例 4	64.0	11.2	15.4	5.7
06	比較例 5	64.3	11.7	10.1	6.1
07	発明例 2	66.0	17.0	30.6	8.0
08	比較例 6	66.2	14.5	26.6	13.5
09	比較例 7	66.6	12.0	9.4	5.7
10	発明例 3	66.6	19.5	26.4	10.8
11	発明例 4	67.2	16.0	27.3	7.8
12	発明例 5	67.2	21.8	42.0	8.3
13	比較例 8	70.0	13.4	11.4	6.5
14	比較例 9	70.2	27.0	44.8	8.3
15	発明例 6	70.4	18.8	45.7	14.0
16	比較例10	74.8	13.7	17.0	6.0
17	発明例 7	78.9	17.3	31.7	11.0
18	比較例11	82.8	13.7	17.0	6.0

【００２９】次に、圧力損失試験装置（図示せず）で、ハニカム構造体１１に、（ａ）空気流量７．５Ｎｍ³／

ｍｉｎとしたときの、流入側１１ｄと流出側１１ｅの差圧、（ｂ）粒径０．０４２μｍのカーボン粉を３ｇ／ｈで２時間投入した後の流入側１１ｄと流出側１１ｅの差圧、（ｃ）触媒を担持した後に、７．５Ｎｍ³／ｍｉｎのときの流入側１１ｄと流出側１１ｅの差圧を測定した。そして、圧力損失（ｍｍＡｑ）を、流入側１１ｄと流出側１１ｅの差圧により求めた。なお、圧力損失の評価は、（ａ）ハニカム構造体１１単独（次の表２では「担体」として示す）については、２３０ｍｍＡｑ未満を優として（◎）、２３０～２５０ｍｍＡｑを良として（○）、２５０ｍｍＡｑを超えるものをＮＧとして（×）で、（ｂ）カーボン粉については、３８０ｍｍＡ＊ｑ未満を優として（◎）、３８０～４００ｍｍＡｑを良として（○）、４００ｍｍＡｑを超えるものをＮＧとして（×）で、（ｃ）触媒については、２８０ｍｍＡｑ未満を優として（◎）、２８０～３００ｍｍＡｑを良として（○）、３００ｍｍＡｑを超えるものをＮＧとして（×）で行った。また、粒径０．０４２μｍのカーボン粉を３ｇ／ｈで２時間投入した後の捕集率（％）を測定した。更に、（社）自動車技術会　自動車規格（ＪＡＳＯ）Ｍ５０５－８７に基づき、ハニカム構造体１１について、Ａ軸の圧縮破壊強度（ＭＰａ）をそれぞれ測定した。その結果を表２に示す。

【００３０】

（表２）

No.	区分	圧力損失の評価			捕集率	A軸圧縮破壊強度
		(a)担体	(b)ｶｰﾎﾞﾝ粉	(c)触媒	(%)	(MPa)
01	比較例 1	×	×	×	100	8.8
02	比較例 2	○	×	×	100	7.0
03	比較例 3	○	×	○	98	6.6
04	発明例 1	◎	○	○	97	5.0
05	比較例 4	×	×	×	100	6.2
06	比較例 5	×	×	×	100	5.6
07	発明例 2	◎	◎	◎	99	3.5
08	比較例 6	◎	×	○	97	5.4
09	比較例 7	×	×	×	100	6.5
10	発明例 3	◎	◎	◎	97	4.2
11	発明例 4	◎	◎	◎	100	4.0
12	発明例 5	◎	◎	◎	96	3.0
13	比較例 8	○	×	○	100	1.8
14	比較例 9	◎	◎	◎	92	0.8
15	発明例 6	◎	◎	○	97	3.6
16	比較例10	○	×	○	98	1.4
17	発明例 7	◎	◎	◎	98	2.8
18	比較例11	○	×	○	97	0.5

【００３１】表２から、発明例１～７は、２０～４０μｍの総細孔容積が全細孔容積の２５％以上、平均細孔径が１５～２５μｍとしていることから、気孔率を６０～８０％と大きくしているにも拘わらず、（ａ）ハニカム構造体１１単独、（ｂ）カーボン粉投入、（ｃ）触媒担持後、何れも圧力損失が少ない。また、発明例１～７は、カーボン粉の捕集率が高く、Ａ軸圧縮破壊強度も確保されている。特に、単位体積あたりのフィルター表面積を７～１３ｃｍ²／ｃｍ³とすることで圧力損失をより少なくすることができる。一方、比較例１～１１は、（ａ）ハニカム構造体１１単独、（ｂ）カーボン粉投入、（ｃ）触媒担持後、の圧力損失、又は、カーボン粉の捕集率、Ａ軸圧縮破壊強度の何れかにおいても十分でなく、問題が残されている。

【００３２】

【発明の効果】以上詳細に説明のとおり、本発明のハニカム構造体によれば、気孔率が大きいにも拘わらず、低圧力損失を維持しつつ、強度を確保し、また排気ガス中の微粒子を高効率に捕集することができる。

【図面の簡単な説明】

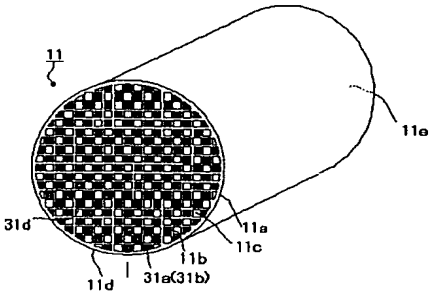
【図１】ハニカム構造体の斜視図である。

【図２】図１のハニカム構造体を用いた排気ガス浄化フィルタ１０の一例の断面模式図である。

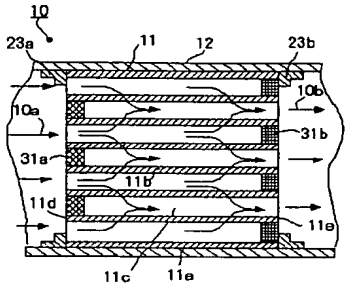
【符号の説明】

１１：ハニカム構造体
１１ａ：外周壁
１１ｂ：セル壁
１１ｃ：セル
１１ｄ：流入側
１１ｅ：流出側
１２：収納容器
２３ａ、２３ｂ：把持部材。

【図１】



【図２】



フロントページの続き

Ｆターム(参考)　3G090 AA02
4D019 AA01 BA05 BA06 BA07 BB06
BD01 CA01 CB04 CB06
4D058 JA38 JB06 JB21 KA11 SA08
4G069 AA01 AA12 BA13A BA13B
EA19 EA25 EC01X EC01Y
EC13X EC13Y EC14X EC18X
EC18Y